

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-264911

(43)Date of publication of application : 26.09.2000

(51)Int.Cl.

C08F 2/50

C08F290/06

// C09D 4/02

(21)Application number : 11-074373

(71)Applicant : NIPPON SHOKUBAI CO LTD

(22)Date of filing : 18.03.1999

(72)Inventor : MATSUKAWA KENJI

INOUE RIE

(54) PHOTOSENSITIVE RESIN COMPOSITION CONTAINING (METHANO) CYCLOHEXENE SKELETON AT END

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition rapidly curing even in air, providing a cured coating film having excellent surface properties such as luster/solid thickness, solvent resistance and adhesivity to a substrate by making the composition include a specific compound, a vinyl ether monomer and a photopolymerization initiator.

SOLUTION: This composition comprises (A) a compound containing two or more (methano)cyclohexane skeletons [preferably (methano) cyclohexenedicarboxylic acid imino group] in one molecule in which at least one skeleton exists at the molecular end, (B) a vinyl ether (preferably an alkyl vinyl ether) and (C) a photopolymerization initiator (preferably photocationic polymerization initiator such as triphenylphosphonium hexafluoroantimonate). The blending ratio A:B of the component A to the component B is preferably 95:5 to 5:95 by weight. The amount of the component C used is 1-10 wt.% based on the total amount of the component A and the component B.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the

[examiner's decision of rejection or application
converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. *** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS**[Claim(s)]**

[Claim 1] A photopolymer constituent characterized by containing a compound (A) with which it has two or more cyclohexene (methano) frames in 1 molecule, and at least one of pieces [them] exists in a molecule end, a vinyl ether monomer (B), and a photopolymerization initiator (C).

[Claim 2] A photopolymer constituent characterized by containing a compound (A'), vinyl ether (B), and a photopolymerization initiator (C) which a compound which has a polymer or oligomer which has two or more functional groups, and this functional group and a functional group which can react, and (methano) has a cyclohexene frame is made to react, and are obtained.

[Claim 3] (Methano) A photopolymer constituent according to claim 1 or 2 whose cyclohexene frame is a cyclohexene (methano) dicarboxylic acid imino group.

[Claim 4] A photopolymer constituent according to claim 1 to 3 said whose photopolymerization initiator (C) is an optical cationic initiator.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION**[Detailed Description of the Invention]**

[0001]

[The technical field to which invention belongs] This invention relates to the photopolymer constituent which hardened promptly also in air, and excelled [paint film / hardening] in front-face nature and solvent resistance, such as gloss and a feeling of a build, in more detail about the photopolymer constituent, and was excellent in adhesion with a substrate.

[0002]

[Description of the Prior Art] Using an unsaturated polyester resin as a photopolymer is well known from the former. However, the paint film by the resin concerned has a slow cure rate, and is inferior to gloss, and since the still more poisonous styrene at the time of hardening may be emitted into atmospheric air, the amelioration is desired from the former.

[0003] Moreover, although using the oligomer which has an acrylic radical as a photopolymer (meta) was also known from the former, when an air anaerobiosis stiffens the oligomer concerned in air strongly, it has the problem from which a hardening paint film front face is un-hardening, and the amelioration was called for strongly.

[0004] As a solution means of the above-mentioned problem, by JP,2-1716,A, unsaturated polyester and the vinyl ether component of ***** are contained, and the liquefied radiation-curing nature constituent with which this vinyl ether component averages per molecule, and has at least two vinyl ether radicals is proposed. Moreover, in the **** No. 505027 [four to] official report, the free radical hardenability constituent which are the mixture of the reagin which has an electronic deficit ethylene system partial saturation end group and a 1 functional-value diluent, or a 1 functional-value diluent, and a free radical hardenability constituent which consists of a 2 functional-value monomer, and has a ratio to the electronic deficit double bond of the electronic richness double bond in this constituent in about 5:1 to 1:5 within the limits is proposed. Furthermore by JP,8-245730,A, the radiation-curing nature constituent containing the unsaturated polyester compound and vinyl ether compound of specific structure is proposed. However, the compound contained in the hardenability constituent these-proposed is a compound of the structure where the cyclohexene frame was incorporated into the molecule. For this reason, it was not what it can still be satisfied with these constituents of in points, such as adhesion with quick hardening in air, and a substrate.

[0005] Moreover, although the resin constituent including the polyester polyvinyl ether which has 2-6 vinyl ether radicals and at least one cyclohexene nucleus in the same molecule, and an optical cationic polymerization catalyst is indicated by JP,5-310811,A, since this also has the structure where the cyclohexene nucleus was similarly incorporated into polymer principal chain structure, it has the defect that copolymerization nature with a vinyl-ether-resin system is bad, therefore inferior to a photoresist.

[0006]

[Problem(s) to be Solved by the Invention] It is in offering the photopolymer constituent which has gloss with the sufficient hardening paint film which hardened the object promptly in smaller quantity of radiation also in air, and was obtained to be able to present practical use, and a feeling of a build, and was excellent in solvent resistance by making this invention in view of the above-mentioned conventional problem, and was excellent in the adhesive property over base material front faces, such as a metal, timber, and plastics.

[0007]

[Means for Solving the Problem] According to this invention, a photopolymer constituent characterized by containing a compound (A) with which it has two or more cyclohexene (methano) frames in 1 molecule, and at least one piece exists in a molecule end before long, a vinyl ether monomer (B), and a photopolymerization initiator (C) is offered.

[0008] Moreover, a photopolymer constituent characterized by containing a compound (A'), vinyl ether (B), and a photopolymerization initiator (C) which a compound which has a polymer or oligomer which has two or more functional groups, and this functional group and a functional group which can react, and (methano) has a cyclohexene frame is made to react, and are obtained according to this invention is offered.

[0009] As for the aforementioned (methano) cyclohexene frame, at this time, it is desirable that it is a cyclohexene (methano) dicarboxylic acid imino group.

[0010] Moreover, as for said photopolymerization initiator (C), it is desirable that it is an optical cationic initiator.

[0011]

[Embodiment of the Invention] Also in air, this invention persons harden promptly and, moreover, a hardening paint film is excellent in front-face nature and solvent resistance, such as gloss and a feeling of a build. And the result of having examined wholeheartedly whether the photopolymer constituent excellent in adhesion with a substrate having been obtained, The compound with which it has two or more cyclohexene (methano) frames in 1 molecule, and at least one of pieces [them] exists in a molecule end, It comes to make header this invention for the photopolymer constituent with which are satisfied of the above-mentioned property being obtained by making a vinyl ether monomer and a photopolymerization initiator contain.

[0012] The details of this invention are explained below. The compound (A) used in this invention has two or more cyclohexene (methano) frames, and if it is a compound with which at least one of pieces [them] exists in the molecule end of a compound, it will not have especially definition. A compound (A) may be a polymer and may be oligomer. Moreover, you may be the mixture. It is that the cyclohexene (methano) frame which exists in a molecule end has reactivity preferably. By making the compound which has the polymer and oligomer which more specifically have two or more functional groups, and this functional group and the functional group which reacts, and has a reactant (methano) cyclohexene frame react, a reactant (methano) cyclohexene frame can be introduced into the end of a polymer or oligomer, and the compound of this invention can be manufactured preferably. As a functional group used in order to introduce a reactant (methano) cyclohexene frame, an epoxy group, an oxazoline radical, an isocyanate radical, an acid-amide radical (aminocarbonyl radical), a carboxyl group, its anhydride radical and hydroxyl, the amino group, an imino group, etc. are mentioned. for example, when the functional groups which said polymer and oligomer have are an epoxy group and an oxazoline radical A cyclohexene carboxylic acid, cyclohexene (methano) dicarboxylic acid, (Methano) The compound which has carboxyl groups, such as cyclohexene tricarboxylic acid, and its anhydride; (Methano) When a functional group is an isocyanate radical The compound which has hydroxyls, such as a hydroxy (methano) cyclohexene; when a functional group is a carboxyl group The compound which has epoxy groups, such as an epoxy (methano) cyclohexene, Or the compound which has hydroxyls, such as a hydroxy (methano) cyclohexene; when a functional group is hydroxyl The compound which has isocyanate radicals, such as 4-isocyanate ethyl (methano) cyclohexene, A cyclohexene carboxylic acid, cyclohexene (methano) dicarboxylic acid, (Methano) The compound which has carboxyl groups, such as cyclohexene tricarboxylic acid, and its anhydride; (Methano) When a functional group is an acid-amide radical The compound which has epoxy groups, such as an epoxy (methano) cyclohexene, Or the compound which has hydroxyls, such as a hydroxy (methano) cyclohexene; when a functional group is an amino group (Methano) The compound which has carboxyl groups, such as a cyclohexene carboxylic acid, cyclohexene (methano) dicarboxylic acid, and cyclohexene (methano) tricarboxylic acid, its anhydride, etc. are mentioned.

[0013] Although the KISEN frame may exist in any of the end of said compound (A), a side chain, and a principal chain frame to reactant (methano) cyclo, in order to obtain quicker hardening, at least one piece needs to exist in the end of said compound.

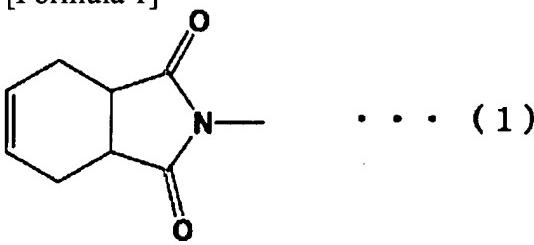
[0014] What is necessary is to be the polymer or compound which especially definition does not have as the polymer which has two or more functional groups, or oligomer, for example, made the main frame polyalkylene imine polymers, such as polyester, a polyether, a polyamide, polyurethane, polyacetal, polyarylate, polyolefine, polyethyleneimine, and

polyamine, a polyene, an acrylic polymer, a styrene system polymer, a phenol polymer, silicone resin, etc., and just to have two or more functional groups. Preferably, if it is these polymers and the polymer with which at least one functional group of oligomer exists in a molecule end, it can use as a raw material which manufactures the compound A of this invention. It is good for there to be two or more functional groups that there are little these polymer and oligomer in the molecule end still more preferably. As this functional group, the epoxy group indicated previously, for example, an oxazoline radical, an isocyanate radical, an acid-amide radical (aminocarbonyl radical), a carboxyl group, hydroxyl, the amino group, an imino group, etc. are mentioned. the viewpoint on workability and a paint film object disposition to weight average molecular weight -- the range of 50-20,000 -- desirable -- the range of 300-10,000 -- the thing of the range of 350-6,000 is still more preferably good.

[0015] As a reactant (methano) cyclohexene frame, if it has the cyclohexene (methano) frame, there will be especially no definition. Especially definition does not have the coupling case, either. For example, a cyclohexene (methano) frame can be introduced through an ester bond by making the polymer which has hydroxyl, and tetrahydro phthalic anhydride and end methylene tetrahydro phthalic anhydride react. Moreover, it is desirable to introduce the cyclohexene frame which is a cyclohexene (methano) frame, and a cyclohexene frame with an end methylene frame through dicarboxylic acid imide association expressed with a general formula (1) and (2), for example in respect of the physical properties of a photoresist paint film. For example, cyclohexene (methano) dicarboxylic acid imino groups, such as the 1-(methano) cyclohexene 1, 2-dicarboxylic acid imino group, the 1-(methano) cyclohexene 1, 4-dicarboxylic acid imino group, the 3-(methano) cyclohexene 1, 2-dicarboxylic acid imino group, the 4-(methano) cyclohexene 1, and 2-dicarboxylic acid imino group, are gestalten desirable in respect of the physical properties of the photoresist paint film of the made photopolymer. Also in this, the 4-(methano) cyclohexene 1 and 2-dicarboxylic acid imino group are desirable. It is 3, the 6-methano-4-cyclohexene 1, and 2-dicarboxylic acid imino group which are the end methylene type shown by the 4-cyclohexene 1 more preferably shown by the following general formula (1), 2-dicarboxylic acid imino group, and the general formula (2). There is especially no definition in the introductory method of these imino groups. Moreover, by for example making alkylene glycol and silicon oligomer, such as diamine compounds, such as a hexamethylenediamine, and a diethylene glycol, and a cyclohexene (methano) carboxylic acid and an anhydride react, the oligomer which has a cyclohexene (methano) frame in a molecule end can be compounded, and it can use as a compound (A) of this invention.

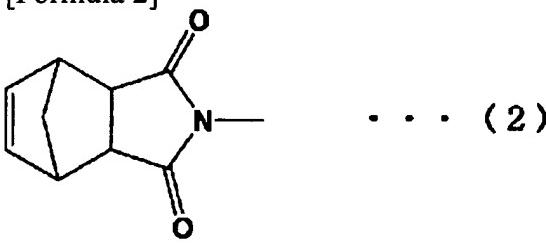
[0016]

[Formula 1]



[0017]

[Formula 2]



[0018] Since the photopolymer constituent of this invention contains the compound (A) with which it has two or more cyclohexene (methano) frames in 1 molecule, and at least one piece exists in a molecule end before long, it is excellent

in curing in air. Moreover, it excels also in adhesion with various base materials.

[0019] As a vinyl ether monomer (B) which can be used by this invention, things polyfunctional also in the thing of one functionality may also be any, and mono-vinyl ether, the divinyl ether, and polyfunctional vinyl ether are mentioned as alkyl vinyl ether. Specifically For example, ethyl vinyl ether, propyl vinyl ether, t-butyl vinyl ether, isobutyl vinyl ether, t-amyl vinyl ether, Dodecyl vinyl ether, octadecyl vinyl ether, butoxy ethyl vinyl ether, 2-ethylhexyl vinyl ether, cyclohexyl vinyl ether, Aminopropyl vinyl ether, 2-diethylamino ethyl vinyl ether, 2-hydroxyethyl vinyl ether, 4-hydroxy butyl vinyl ether, 6-hydroxy hexyl vinyl ether, 1, 4-cyclohexane dimethanol mono-vinyl ether, Mono-vinyl ether, such as phenyl vinyl ether; The divinyl ether, The 1,4-butanediol divinyl ether, the 1,6-hexanediol divinyl ether, 1, 4-cyclohexane dimethanol divinyl ether, the ethylene glycol divinyl ether, The diethylene-glycol divinyl ether, the triethylene glycol divinyl ether, The tetraethylene glycol divinyl ether, the polyethylene-glycol divinyl ether, The propylene glycol divinyl ether, the dipropylene glycol divinyl ether, The tripropylene glycol divinyl ether, the tetrapropylene glycol divinyl ether, The divinyl ether, such as the polypropylene-glycol divinyl ether; The trimethylol propane TORIBI nil ether, The pentaerythritol tetravinyl ether, the pentaerythritol TORIBI nil ether, Polyfunctional vinyl ether, such as vinyl-ether-izing hydroxyl in dipentaerythritol hexa vinyl ether or the methylol radical of tricyclodecanedimethylol, and being obtained, is mentioned. Moreover, of course, vinyl ether other than this can also be used as a vinyl ether monomer (B) of this invention. Aromatic series vinyl ether, such as phenyl vinyl ether and the dihydroxybenzene divinyl ether; polyvinyl ether, polyester vinyl ether, etc. of phenol resin, such as a vinyl ether derivative, can be mentioned as a vinyl ether derivative of resin. independent in these -- or two or more kinds can use it, mixing. Also in these, it is desirable to use alkyl vinyl ether, such as mono-vinyl ether, the divinyl ether, and polyfunctional vinyl ether, from the point of reducibility and hardening paint film physical properties.

[0020] Although especially the mixed rate of a compound (A) and a vinyl ether monomer (B) of having two or more cyclohexene (methano) frames in 1 molecule is not limited, it is desirable the range of (A):(B)=95:5-5:95 and that it is in the range of 90:10-40:60 more preferably by the weight ratio from a viewpoint of good activity viscosity and material physical properties.

[0021] As an amount of installation of the cyclohexene frame in the compound (A) (methano) with which it has two or more cyclohexene (methano) frames in 1 molecule, and at least one of them exists in a molecule end As for the molecular weight which is per [which is contained in a compound (A) from a viewpoint of the balance of a photoresist and hardening paint film physical properties (methano)] cyclohexene frame, 100-10,000 are desirable, and especially 250-3,000 are [200-5,000 are more desirable and] still more desirable.

[0022] Although it will not be limited especially if it has the capacity to make copolymerization of the polymerization nature unsaturated bond of the cyclohexene (methano) frame origin, and vinyl ether start according to an operation of light, as a photopolymerization initiator (C) which can be used by this invention, the so-called optical cationic initiator which decomposes by light and generates a cation kind can use it suitably in respect of improvement in a cure rate. As a concrete example of this cation photopolymerization initiator, the onium salt of Lewis acid, such as triphenyl phosphonium hexafluoroantimonate, triphenyl phosphonium hexafluorophosphate, p-(phenylthio) phenyl diphenyl sulfonium hexafluoroantimonate, 4-KURORU phenyl diphenyl sulfonium hexafluorophosphate, and [(2, 4-cyclopentadiene-1-IRU) (1-methylethyl) benzene]-iron-hexafluorophosphate, is mentioned. these photopolymerization initiator -- for example, the Asahi electrification company make -- "OPTOMER SP- 150, 170, and ULTRASET" -- SAN-AID SI-60L, "80L, 100L" by 3 Japanese Federation of Chemical Industry Workers' Unions, "CI series" by Nippon Soda Co., Ltd., "KAYACURE PCI-204,205,615,625" by Nippon Kayaku Co., Ltd., Union Carbide "CYRACURE UVI-6974, UVI-6990", "Photoinitiator2074" by Rhone Poulenc S.A., "AMERICURE" by the Toshiba Silicone "UV-9310C" American can company, the "UVE series" by the general electric company, the Ciba-Geigy "IRUGA cure -261", etc. are available as a commercial item.

[0023] Moreover, as other photopolymerization initiators, the compound which generates a free radical according to an operation of light is available. As this optical radical polymerization initiator, for example 4-phenoxy dichloro acetophenone, A 4-t-butyl-dichloro acetophenone, a 4-t-BUCHIRUTORIKURORO acetophenone, A diethoxy acetophenone, 2-hydroxy - 2-phenyl-1-phenyl propane-1-ON, 1-(4-dodecyl phenyl)-2-hydroxy-isobutane-1-ON, 1-(4-isopropyl phenyl)-2-hydroxy-isobutane-1-ON, 4 -(2-hydroxy ethoxy)- Phenyl-(2-hydroxy-2-propyl) ketone, 1-hydroxy

cyclohexyl phenyl ketone and 2-methyl -- the acetophenone system compound; benzoin of -1-[4-(methylthio) phenyl]-2-morpholino propane-1 grade -- Benzoin methyl ether, benzoin ethyl ether, benzoin iso-propyl ether, Benzoin system compounds, such as benzoin isobutyl ether and benzyl dimethyl ketal; A benzophenone, Benzoylbenzoic acid, methyl o-benzoylbenzoate, 4-phenylbenzo phenon, A hydroxy benzophenone, an acrylic-ized benzophenone, 4-benzoyl-4'-methyl diphenyl sulfide -3, 3'-dimethyl-4-methoxybenzophenone, A - dimethylamino benzophenone, and 4 and 4' 4, 4'-diethylamino benzophenone, Benzophenone system compounds, such as 3, 3', 4, and a 4'-tetrapod (tert-butyl peroxide carbonyl) benzophenone; A thioxan ton, 2-chloro thioxan ton, 2-methylthio xanthone, 2, 4-dimethyl thioxan ton, 2, 4-diethyl thioxan ton, 2, 4-diisopropyl thioxan ton, An isopropyl thioxan ton, a 1-chloro-4-propoxy thioxan ton, Thioxan ton system compound;alpha-ASHIROKI SIMM ester, such as 2 and 4-dichloro thioxan ton, Methylphenylglyoxylate, benzyl, 9, 10-phenanthrene quinone, A camphor quinone, dibenzosulfone, 2-ethyl anthraquinone, 4', ketone system compound [, such as 4"-diethyl isophthalophenone,]; A 2 and 2'-screw Imidazole system compounds, such as (2-chlorophenyl)-4, 4', 5 and the 5'-tetrapod phenyl -1, and a 2'-imidazole; Acyl phosphine oxide system compound [, such as 2, 4, and 6-trimethyl benzoyl diphenylphosphine oxide]; In addition, a carbazole system compound etc. is mentioned.

[0024] These photopolymerization initiators (C) can be used combining respectively independent or two kinds or more. Moreover, the amount of the photopolymerization initiator (C) used has 0.1 - 30% of the weight of a desirable range to the AUW of the compound (A) which has two or more cyclohexene (methano) frames in 1 molecule, and a vinyl ether monomer (B). In addition, the amount of the photopolymerization initiator (C) used has 2 - 5% of the weight of a range more preferably desirable in order to keep the hue of a hardened material good, without reducing a photoresist greatly one to 10% of the weight to the AUW of a compound (A) and a vinyl ether monomer (B).

[0025] Moreover, in order to raise the hardenability of the photopolymer constituent of this invention further, a heat radical generating agent may be blended if needed. As a heat radical generating agent, sensitizers, such as triethylamine, diethylamine, diethanolamine, ethanolamine, a dimethylamino benzoic acid, dimethylamino methyl benzoate, a thioxan ton, 2-isopropyl thioxan ton, 2, 4-diethyl thioxan ton, and an acetylacetone, a benzoyl peroxide, azobisisobutyronitril, etc. are mentioned.

[0026] The features of another photopolymer constituent of this invention are the compound (A") which has a cyclohexene frame at least, and a constituent containing a vinyl ether monomer (B) and a photopolymerization initiator (C), and a compound (A") is in the point that the measured value of the amount of the minimum UV irradiation which is the scale which shows hardenability is below 180 (mj/cm²). The amount of the minimum UV irradiation here The compound (A") 70 section, the vinyl ether (monomer B) 30 section, The resin constituent which consists of the photopolymerization (initiator C) 3 section is applied so that it may become the humid thickness of 15 micrometers on a glass substrate using a bar coating machine. Subsequently, it exposes using the black light (distance with the light source: 10cm) equipped with the high-pressure mercury lamp of 80 W/cm, a paint film front face is checked by *****, and an ultraviolet radiation dose until adhesiveness disappears is said.

[0027] This amount value of the minimum UV irradiation is below 50 (mj/cm²) most preferably the 70 (mj/cm²) following still more preferably the 100 (mj/cm²) following more preferably [below 150 (mj/cm²) is desirable and]. It means hardening with small light energy, so that the amount of the minimum UV irradiation so needs big light energy for hardening that the value is large and the value is small. Moreover, it means that a cure rate is also so quick that the amount of the minimum UV irradiation is small. Therefore, it is so desirable that the amount of the minimum UV irradiation is small as a photopolymer.

[0028] The compound which the compound which has the polymer or oligomer which has two or more functional groups, and this functional group and the functional group which can react as such a compound (A") that has a cyclohexene frame at least, and (methano) has a cyclohexene frame is made to react, and is obtained has, and has two or more cyclohexene frames in a monad more preferably, and has at least one of them in the molecule end is mentioned. [desirable]

[0029] Various kinds of thermal polymerization inhibitors, a leveling agent, a thickener, an adhesiveness-reducing agent, a thixotropy grant agent, an antihalation agent, a flattening, an ultraviolet ray absorbent, a color pigment, a diluent, a filler, a reinforcement, thermoplastics, etc. may be blended with the photopolymer constituent of this invention within limits which do not fall a photoresist remarkably.

[0030] moreover, in the range which does not check an effect of the invention, other photopolymerization nature resin, for example, a photosensitive epoxy resin, an oxetane compound, acrylic urethane resin, an unsaturated polyester resin, etc. may be mixed at a rate which is arbitration.

[0031] The photopolymer constituent of this invention can be stiffened by the conventionally well-known photo-curing method, such as ultraviolet curing and electron ray hardening. For example, when based on ultraviolet curing, the resin constituent of this invention is first applied to a base material, after carrying out evaporation desiccation of the solvent and volatile component which are contained in resin, fixed time amount exposure is carried out as the light source, and a medium-voltage mercury lamp etc. is stiffened. If it fully hardens, and a tuck free-lancer's hardening paint film is obtained for a short time and it is made to harden in inert gas, such as nitrogen and an argon, even if the ambient atmosphere at the time of photo-curing is dry air, hardening paint film engine performance, such as a water resisting property and chemical resistance, will improve further. Moreover, the so-called postbake process which reheats to a suitable temperature after photo-curing is performed, even if it raises paint film physical properties further, it is, and it is **. There is especially no definition and it should just determine suitably the method of application to a base material, the class of light source, the exposure method, etc. in consideration of a compound, the class of a vinyl ether monomer and photopolymerization initiator, loadings, an operating environment, etc.

[0032] Thus, the photopolymer constituent of obtained this invention can be used for the adhesives which can be used for the coating material for [, such as timber, paper, a particle board, a metal, plastics, glass, concrete, asphalt, and a ceramic,] base materials, a water blocking material use, paint resin, putty, a sealing agent, various base materials, etc., the resin for anchoring agents, a printing ink binder, the resin for the Mitsuzo forms, the resin for solder resists, the resin for photoresists, the resin for the printing versions,

[0033]

[Example] An example explains this invention still more concretely below. In addition, this invention is not limited to these examples, and the "weight section" is meant unless the inside of an example and the "section" have a notice especially.

[0034] it cool, after add 3, the 6-methano-4-cyclohexene -1, the 2-dicarboxylic acid 328 section, the liquid polybutadiene (product made from ARCO "Poly-bdR-45M"; hydroxyl equivalent 1750) 3500 section that have a hydroxyl end, and the triethyl benzyl ammonium chloride 19 section to the 51. 4 opening flask equipped with example of resin composition 1 stirrer, the thermometer, the reflux cooling pipe, and the nitrogen gas installation pipe and make it react to it at 110 degrees C under a nitrogen air current for 5 The polybutadiene 3847 section which introduced the anhydride of 3, the 6-methano-4-cyclohexene -1, and 2-dicarboxylic acid into the end of the polymer through the half ester bond was obtained. Let the obtained resin be resin 1.

[0035] The anhydride 304 section of the 4-cyclohexene -1 and 2-dicarboxylic acid was added to the 500ml 4 opening flask equipped with example of resin composition 2 stirrer, the thermometer, the reflux cooling pipe, the tap funnel, and the nitrogen gas installation pipe, and it heated to 110 degrees C under the nitrogen air current, and considered as the liquid. Subsequently, it was dropped over 2 hours at this temperature, noticing about pyrexia the hexamethylenediamine (liquid) 116 section warmed at 50 degrees C from the tap funnel. Changed the reflux cooling pipe for the fractionating tower after dropping termination, carry out temperature up gradually to 200 degrees C, and it was made to react at this temperature further for 4 hours, after checking that the condensation water of the 35 sections had distilled, it cooled, and the oligomer 384 section which the 4-cyclohexene -1 and 2-dicarboxylic acid imino group combined with both ends through the hexamethylene radical was obtained. Let the obtained resin be resin 2.

[0036] The anhydride 328 section of 3, the 6-methano-4-cyclohexene -1, and 2-dicarboxylic acid and the N.N-dimethylformamide 150 section were added to the 11. 4 opening flask equipped with example of resin composition 3 stirrer, the thermometer, the reflux cooling pipe, the tap funnel, and the nitrogen gas installation pipe, and it heated to 80 degrees C under the nitrogen air current, and considered as the solution. Subsequently, it was dropped over 2 hours at this temperature, noticing the 50 % of the weight solution of N.N-dimethylformamide of the glycine (aminoacetic acid) 150 section about pyrexia from a tap funnel. Changed the reflux cooling pipe for the fractionating tower after dropping termination, carry out temperature up gradually to 200 degrees C, and it was made to react at this temperature further for 3 hours, after checking that the condensation water and N.N-dimethylformamide of the 336 sections had distilled, it

cooled, and the N-carboxymethyl -3, 6-methano-4-cyclohexene -1, and 2-dicarboxylic acid imide 442 section was obtained.

[0037] Added the succinic anhydride 200 section, the diethylene glycol 318 section, and the dibutyl tin oxide 0.1 section, carry out temperature up to the 11. 4 opening flask equipped with the stirrer, the thermometer, the fractionating tower, and the nitrogen gas installation pipe gradually to 210 degrees C under a nitrogen air current, and it was made to react to it at this temperature further apart from this for 7.5 hours, after check that the condensation water of the 36 sections had distilled, it cooled, and the polyester polyol 482 section of the acid number 1.3 was obtained. Then, added the N-carboxymethyl [which was compounded previously] -3, 6-methano-4-cyclohexene -1, and 2-dicarboxylic acid imide 442 section to the flask, carry out temperature up to 210 degrees C under a nitrogen air current, and it was made to react at this temperature further for 11 hours, after checking that the condensation water of the 36 sections had distilled, it cooled, and the polyester 888 section of 3, the 6-methano-4-cyclohexene -1, and 2-dicarboxylic acid Let the obtained resin be resin 3.

[0038] The method same with the 11. 4 opening flask equipped with example of resin composition 4 stirrer, the thermometer, the reflux cooling pipe, the tap funnel, and the nitrogen gas installation pipe as the example 3 of resin composition The N-carboxymethyl [which was obtained] -3, 6-methano-4-cyclohexene -1, 2-dicarboxylic acid imide 442 section, 1, and 3-screw (glycidoxyl propyl) tetramethyl disiloxane 362 section and the triethyl benzyl ammonium chloride 4 section were added, after making it react at 90-120 degrees C under a nitrogen air current for 6 hours, it cooled, and the silicone oligomer 808 section of 3, the 6-methano-4-cyclohexene -1, and 2-dicarboxylic acid imide end was Let the obtained resin be resin 4.

[0039] The triethylene glycol 150 section and the dibutyl tin JIRAU rate 0.2 section were added, and it heated to 50 degrees C under the nitrogen air current, and it was dropped at the 500ml 4 opening flask equipped with example of comparison resin composition 1 stirrer, the thermometer, the reflux cooling pipe, the tap funnel, and the nitrogen gas installation pipe over 2 hours at this temperature, noticing the hexamethylene di-isocyanate 252 section about pyrexia from a tap funnel. Temperature up of the ** within after dropping termination was carried out to 75 degrees C, and it agitated at this temperature further for 1 hour, and it was dropped over 1 hour at this temperature, having noticed inside ** about 50 degrees C, and noticing the 2-hydroxyethyl acrylate 116 section about pyrexia from lowering and a tap funnel again. It cooled, after carrying out temperature up of the ** within after dropping termination to 75 degrees C and agitating at this temperature further for 3 hours, and the acrylic urethane resin 518 section was obtained. Let the obtained resin be resin 5.

[0040] The maleic-anhydride 294 section, the diethylene-glycol 212 section, and the trimethylol propane diaryl ether 428 section are added to example of comparison resin composition 2 stirrer, a thermometer, a fractionating tower, and the 11. 4 opening flask equipped with the nitrogen gas installation pipe, and it is 190 degrees C under a nitrogen air current. Carry out temperature up gradually and it was made to react at this temperature further for 8 hours, after checking that the condensation water of the 54 sections had distilled, it cooled, and the polyester 880 section which has the allyl— compound ether unit of the acid number 18 was obtained. Let the obtained resin be resin 6.

[0041] The example of comparison resin composition 3 tetrahydrophthal acid dichloride 104 section and the methylene chloride 1350 section were taught, and temperature control was carried out to 25 degrees C, and it agitated.

Subsequently, the mixture of the triethylene glycol mono-vinyl ether 176 section, the triethylamine 156 section, the 4-dimethylaminopyridine 1.8 section, and the methylene chloride 2250 section was dropped over about 2 hours at this temperature, it agitated for further 1 hour, and the reaction was ended. Subsequently, after washing a reaction mixture 3 times in the mixed aqueous solution 4000 section of 440g of water, 10g of phosphoric acids, 25g of sodium hydrogencarbonates, and 25g of salt, the solvent was distilled off under reduced pressure and the vinyl ether derivative which has a cyclohexene nucleus in a molecule was obtained. Let the obtained resin be resin 7.

[0042] The anhydrous tetrahydrophthal acid 456 section, the diethylene-glycol 212 section, and the trimethylol propane diaryl ether 428 section are added to example of comparison composition 4 stirrer, a thermometer, a fractionating tower, and the 11. 4 opening flask equipped with the nitrogen gas installation pipe, and it is 190 degrees C under a nitrogen air current. Carry out temperature up gradually and it was made to react at this temperature further for 14 hours, after checking that the condensation water of the 54 sections had distilled, it cooled, and the polyester 1042 section which has

the allyl compound ether unit of the acid number 9 was obtained. Let the obtained resin be resin 8.

[0043] In addition, the weight average molecular weight (polystyrene standard) using the gel permeation chromatography (GPC) of the resin obtained above is as follows.

Resin 1 (example 1 of resin composition) :Mw=4,900 resin 2 (example 2 of resin composition) : Mw=400 resin 3 (example 3 of resin composition) : Mw=1,100 resin 4 (example 4 of resin composition) :Mw=850 resin 5(example 1 of comparison resin composition):Mw=1,200 resin 6(example 2 of comparison resin composition):Mw=1,290 resin 7 (example 3 of comparison resin composition):Mw=610 resin 8(example 4 of comparison resin composition):Mw=1,930

[0044] Each component is mixed to the resin 1-8 obtained by examples 1-6 and the example 1 of a comparison - the examples 1-4 of the 11 above-mentioned resin manufacture, and the examples 1-4 of comparison resin manufacture at a rate (however, the numeric character in a table is the weight section) shown in tables 1 and 2, a resin constituent is prepared to it, and the result of the hardenability of each resin constituent, gloss, MEK rubbing, and an adhesion test is shown in In addition, it is as [measuring method / of the various properties of the resin constituent in the following examples and examples of a comparison] follows. in addition, each measurement -- the constant temperature of 25 degrees C and 65%RH -- it carried out by constant humidity.

[0045] (Hardenability) The constituent was applied so that it might become the humid thickness of 15 micrometers on a glass substrate using a bar coating machine, and it exposed using the black light (distance with the light source: 10cm) subsequently equipped with the high-pressure mercury lamp of 80 W/cm. The paint film front face was checked by ****, and the ultraviolet radiation dose until adhesiveness disappears was measured. In each measured value in a table, a constituent with few ultraviolet radiation doses means excelling in hardenability.

[0046] (Gloss) The constituent was applied so that it might become the humid thickness of 15 micrometers on a glass substrate using a bar coating machine, ultraviolet radiation was irradiated using the black light (distance with the light source: 10cm) subsequently equipped with the high-pressure mercury lamp of 80 W/cm, and the hardening paint film was obtained. Visual assessment of the gloss of the obtained paint film was carried out. That from which, as for what is excellent in gloss, "O" and gloss fall a little made "x" the thing without "****" and gloss (it becomes a letter of grinding).

[0047] (MEK rubbing) The constituent was applied so that it might become the humid thickness of 15 micrometers on a glass substrate using a bar coating machine, the ultraviolet radiation of 2000 mJ/cm² was irradiated using the black light (distance with the light source: 10cm) subsequently equipped with the high-pressure mercury lamp of 80 W/cm, and the hardening paint film was obtained. The obtained paint film was eventually ground against the gauze into which the methyl ethyl ketone (MEK) was infiltrated to 50 times by a unit of 10 times, and visual assessment of the gloss on the front face of a paint film was carried out (gauze was counted with 1 time by going one time). That from which, as for that from which gloss does not change, "O" and gloss fall a little made "x" that "****" and whose gloss are completely lost.

[0048] (Adhesion) The constituent was applied so that a bar coating machine might be used and it might become the humid thickness of 15 micrometers on each base material, the ultraviolet radiation of 2000 mJ/cm² was irradiated using the black light (distance with the light source: 10cm) subsequently equipped with the high-pressure mercury lamp of 80 W/cm, and the hardening paint film was obtained. The Scotch tape (Nichiban Co., Ltd. make) was stuck on the obtained paint film (pasting area: 18mmx20mm), and the tape friction test was performed. That in which a paint film did not exfoliate took as "****", and what exfoliated altogether was taken as "x" about "O" and the thing which exfoliated selectively. In addition, as a base material, the dull steel sheet, the rigid-polyvinyl-chloride board, and the China plywood were used.

[0049]

[A table 1]

| | 実施例1 | 実施例2 | 実施例3 | 実施例4 | 実施例5 | 実施例6 |
|-----------------------------|----------|----------|----------|----------|----------|----------|
| 使用樹脂 | 樹脂1 | 樹脂2 | 樹脂2 | 樹脂3 | 樹脂3 | 樹脂4 |
| 樹脂量(部) | 50 | 80 | 80 | 70 | 70 | 65 |
| TEG-DVE(部) | 50 | — | — | — | — | 35 |
| n-BuVE(部) | — | 20 | 20 | — | — | — |
| i-BuVE(部) | — | — | — | 30 | 30 | — |
| TMPTA(部) | — | — | — | — | — | — |
| SM(部) | — | — | — | — | — | — |
| Irugacure 261(部) | 3 | 3 | — | 3 | — | 3 |
| Darocur 1173(部) | — | — | 3 | — | 3 | — |
| 硬化性 (mJ / cm ²) | 70 | 50 | 70 | 50 | 70 | 70 |
| 光沢 | ○ | ○ | ○ | ○ | ○ | ○ |
| MEKラビング | 50回 ○ | 50回 ○ | 50回 ○ | 50回 ○ | 50回 ○ | 50回 ○ |
| 密着性 | — | — | — | — | — | — |
| ダル鋼板 | ○ | ○ | ○ | ○ | ○ | ○ |
| 硬質塩化ビニル板 | ○ | ○ | ○ | ○ | ○ | ○ |
| シナ合板 | ○ | ○ | ○ | ○ | ○ | ○ |

[0050]

[A table 2]

| | 比較例1 | 比較例2 | 比較例3 | 比較例4 | 比較例5 | 比較例6 | 比較例7 | 比較例8 | 比較例9 | 比較例10 | 比較例11 |
|-----------------------------|----------|----------|----------|----------|------|------|----------|------|------|----------|----------|
| 使用樹脂 | 樹脂5 | 樹脂6 | 樹脂7 | 樹脂7 | 樹脂1 | 樹脂1 | --- | --- | --- | 樹脂8 | 樹脂8 |
| 樹脂量(部) | 70 | 70 | 100 | 70 | 100 | 100 | — | — | — | 70 | 70 |
| TEG-DVE(部) | — | — | — | — | — | — | 100 | 100 | 30 | 30 | 30 |
| n-BuVE(部) | — | — | — | — | — | — | — | — | — | — | — |
| i-BuVE(部) | — | — | — | — | — | — | — | — | — | — | — |
| TMPTA(部) | 30 | — | — | 30 | — | — | — | — | — | — | — |
| SM(部) | — | 30 | — | — | — | — | — | — | 70 | — | — |
| Irugacure 261(部) | — | — | — | — | 3 | — | 3 | — | 3 | — | 3 |
| Darocur 1173(部) | 3 | 3 | 3 | 3 | — | 3 | — | 3 | — | 3 | — |
| 硬化性 (mJ / cm ²) | 70 | 500 | 300 | 200 | 硬化せず | 硬化せず | 90 | 硬化せず | 硬化せず | 700 | 900 |
| 光沢 | ○ | △ | ○ | △ | --- | --- | ○ | --- | --- | △ | △ |
| MEKラビング | 50回 △ | 30回 × | 50回 ○ | 30回 × | --- | --- | 50回 △ | --- | --- | 30回 × | 50回 ○ |
| 密着性 | — | — | — | — | — | — | — | — | — | — | — |
| ダル鋼板 | △ | × | ○ | × | --- | --- | × | --- | --- | × | ○ |
| 硬質塩化ビニル板 | × | × | ○ | △ | --- | --- | ○ | --- | --- | × | ○ |
| シナ合板 | ○ | △ | △ | △ | --- | --- | ○ | --- | --- | △ | ○ |

[0051] TEGDVE:triethylene glycol divinyl ether n-BuVE:n-butyl vinyl ether i-BuVE:i-butyl vinyl ether TMPTA: -- trimethylolpropane triacrylate -- the optical radical polymerization initiator by optical cationic initiator

Darocur1173:Merck Co. by SM:styrene monomer THPA:tetrahydro phthalic anhydride Irugacure261:Ciba-Geigy [0052]

According to each assessment result in tables 1 and 2, photo-curing of the resin constituent of the examples 1-6 which are the resin constituents of this invention was carried out promptly, and the hardening paint film was excellent in gloss, solvent resistance, and adhesion. Adhesion [as opposed to a rigid-polyvinyl-chloride board at the example 1 of a comparison, on the other hand, using the acrylic urethane resin constituent] was poor. In the example 2 of a comparison using the polyester resin constituent which has an allyl compound ether unit, hardening took long duration, and gloss was completely lost in the MEK rubbing trial at 30 times, and adhesion was also poor with the dull steel sheet and the rigid-polyvinyl-chloride board. In the example 3 of a comparison using the vinyl ether derivative which has a cyclohexene nucleus in a molecule, although gloss, MEK rubbing, and adhesion showed the comparatively good result, hardening

took the energy of 300 mJ/cm². In the example 4 of a comparison which added trimethylolpropane triacrylate further, hardening took the energy of 200 mJ/cm² using the same vinyl ether derivative as the example 3 of a comparison, and the adhesion to MEK rubbing and a dull steel sheet was poor. In the examples 5 and 6 of a comparison, although the photopolymerization initiator was added to the compound which has two or more cyclohexene frames in a molecule, it did not harden. Moreover, in the example 7 of a comparison which made vinyl ether add and harden an optical cationic initiator, the adhesion to a dull steel sheet was poor. The hardening reaction did not occur in the example 8 of a comparison which added the optical radical polymerization initiator to vinyl ether. The hardening reaction did not occur in the example 9 of a comparison which added the optical cationic initiator in vinyl ether and styrene, either.

[0053] Moreover, in the examples 10 and 11 of a comparison which added the optical radical polymerization initiator or the optical cationic initiator, the gloss of hardenability is poor into the mixture of the compound and vinyl ether which have two or more cyclohexene frames in intramolecular, and MEK rubbing and adhesion were also inferior to it by optical radical hardening (example 10 of a comparison).

[0054]

[Effect of the Invention] Gloss with the hardening paint film sufficient with quantity of radiation small also in air according to this invention which hardened promptly and was obtained to be able to present practical use, and a feeling of a build The photopolymer constituent which has, and was excellent also in solvent resistance, and was further excellent in the adhesive property over base material front faces, such as a metal, timber, and plastics, is obtained, and it can use for the coating material for [, such as timber, paper, a particle board, a metal, plastics glass, concrete, asphalt, and a ceramic,] base materials, paint resin, putty, a sealing agent, adhesives, a printing ink binder, the resin for the Mitsuzo forms, the resin for solder resists, the resin for

[Translation done.]